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EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

THE RETENTION OF ORGANIC AND INORGANIC COMPOUNDS ON CLAY MINERALS

Part II : The Interaction of Attapulgus Clay and Polyphenylic Nuclear Reactor Coolants

by

R. LOPES CARDOZO and D. VAN VELZEN

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ORGEL Program

Joint Nuclear Research Center
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SUMMARY

The interaction of Attapulgus Clay and polyphenylic reactor coolants is shwon to consist of irreversible chemisorption of oxygen containing compounds present in the highest molecular weight part of the coolant.

The concentration of these compounds is estimated as 1-2 % w.

The saturation capacity of Attapulgus Clay is limited to approximately 5-10 % w.

A reaction mechanism, comprising diffusion, adsorption and reaction, is proposed. The involed set of equations is solved for the case that the resistance due to adsorption is negligible. Numerical values for the rate constants are determined. Experimental data are satisfactorily in agreement with the theoretical model.

KEYWORDS

CLAYS
ORGANIC COOLANT
POLYPHENYLS
CHEMISORPTION
OXYGEN COMPOUNDS
SATURATION
REACTION KINETICS
DIFFUSION
ADSORPTION
EQUATIONS
NUMERICALS

CONTENTS

THE RETENTION OF ORGANIC AND INORGANIC COMPOUNDS ON CLAY MINERALS(+)

1. INTRODUCTION

One of the major problems in the development of an organic cooled reactor is the control of fouling on fuel elements. A process proposed for the elimination of fouling inducing constituents, is sorption on Attapulgus Clay.

This clay material is frequently used in industry under the name "Fuller's earth". Its main constituent is a hydrous aluminium silicate, the clay mineral "attapulgite". An extensive study of relevant fundamental properties of Attapulgus Clay has recently been accomplished (1).

With Attapulgus Clay, some promising results have been obtained in batch experiments in the United States and Canada (2) (3). As a result of these studies, Attapulgus sorption systems were installed and operated in a bypass loop at the OMRE during Core III-B and III-C (3), in the U-3 and X-7 loop at Chalk River and in the WR-1 reactor at Pinawa (A.E.C.L.).

During operation of Core III-B and C the impurity level of the coolant was very low. However, in this case purification was not performed by sorption only; distillation (at a fairly high rate) and filtration techniques were applied concurrently. This makes it impossible to determine the extent to which Attapulgus Clay treatment may have contributed to the good performance of the fuel-coolant system. The experiments carried out at Chalk River and Pinawa do not provide very coherent results either.

Strictly speaking, until now it has not been proved whether the installation of Attapulgus columns in reactor coolant purification circuits is useful or not.

It was therefore of interest to investigate with greater thoroughness the reaction rate, the nature of the reacting impurities and the maximum sorption capacity of Attapulgus Clay.

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2. NATURE OF THE REACTING IMPURITIES

2.1. Oxygen and HHB content

It has been observed that Attapulgus Clay treatment of spent coolants often improves the colour. This change of colour from darkbrown, almost black, to a much lighter brown, is most pronounced when the ratio coolant/clay is low, or, in case of percolation, in the first percolation fractions. Obviously, the most intensely coloured impurities are adsorbed.

In organic chemistry intensely dark coloured impurities are usually of a high molecular weight and often oxygen-containing. This gives rise to the anticipation that in the present case the adsorbed products will also, at least partly, consist of high molecular, oxygen-containing compounds.

To check on these points, an arbitrary method for the determination of high molecular compounds in terphenyl coolants (in future called Heavy High Boilers = HHB) has been developed. The analysis has been derived from the Differential Solubility Method for coolant reclamation (5), (6). This method consists of a fractionation of the coolant by solvent treatment into a soluble, relatively low molecular weight portion and an insoluble, solid, high molecular weight residue, the HHB.

In the course of the present study, n-decane has been selected as a suitable solvent; the process is carried out at room temperature. The analytical procedure is given in the Appendix.

With the aid of this method of analysis, the nature of the sorbed products was investigated by some experiments in which a coolant was percolated over a bed of Attapulgus Clay in glass or stainless steel columns.

The HHB content of the orginal product and of a number of the percolation fractions was determined. Data, results and conditions of these experiments are given in Table I, III and Fig. 8.

In all cases, especially for the first fractions, a notable decrease in HHB content upon Attapulgus Clay treatment is observed. The effect decreases rapidly with increasing contact time.

The oxygen content of terphenyl coolants before and after percolation over Attapulgus Clay was determined in a few other experiments, of which data, conditions and results are given in Table II and III. The oxygen content of the various samples was determinated by the reaction O^{16} (n, p) N^{16} by means of 14 MeV neutrons from a neutron generator (7). The results unanimously show a marked decrease in oxygen content of coolants upon Attapulgus treatment.

The combined data for oxygen sorption on Attapulgus Clay are plotted in Fig. 1, giving the quantity of sorbed oxygen against the total oxygen throughput. Sorption data, of which the errors due to the inaccuracy of the analysis exceeded $\pm$ 200% of the total value, have been discarded (see Table IV).
It follows from Fig. 1 that the saturation capacity of Attapulgus Clay lies between 1500 and 3500 mg/kg of oxygen.

The data given in Table I and II show either the sorption of HHB or of oxygen containing compounds and the results of Table III show incontrovertibly that these two effects appear concurrently. It is therefore concluded that high-molecular, at least partly oxygen-containing compounds are preferentially retained on Attapulgus Clay.

From the data of Table I, II and III the oxygen content of the active impurities can be estimated to be 3-5%w.

2.2. Fouling Tendency

A standard fouling test has been performed with a large number of fractions from the percolation runs carried out in 4 cm Ø stainless steel column (Table I).

This test consists of determination of the weight of deposits precipitated

in 24 h on an electrically heated wire (temperature 520-550°C) in a standard cell containing about 150 g of coolant (8).

The results of the fouling tests are not very conclusive. Most probably the induced effects are of the same order of magnitude as the reproducibility of the test. It can only be concluded that Attapulgus treatment tends to decrease the fouling tendency to some extent, a conclusion that has been drawn before by other investigators (2), (3).

The observed reduction of the fouling tendency may very well be explained by sorption on the clay of high molecular, oxygen containing compounds, since these compounds are generally believed to be to a high degree responsible for the appearance of fouling layers.

3. THE NATURE OF THE SORPTION PROCESS

3.1. Irreversibility

It is an intrinsic property of physical adsorption that the quantity of sorbate retained depends on the concentration in solution. This implies that the sorbed impurities are removed from the sorbent on extensive elution with pure solvents. It has been investigated if Attapulgus Clay in contact with polyphenyl coolants also showed this phenomenon. To this end, elution of the spent clay from the percolation experiment A 229 (Table I) has been carried out. After termination of this percolation run, 100 ml pure OM-2 were passed through the column. The last fractions of eluate had practically the same yellow colour as virginal OM-2.

From the total eluate all the terphenyl was distilled off at 15 mm Hg, 250°C. This residue (11.3 g) consists of High Boilers from interstitial coolant still present at the start of the elution and of the sorbate removed from the clay by the elution. It has been proved above, that the sorbate consists greatly of HHB, so that, if any appreciable amount of sorbate is removed, the above residue must contain more HHB than the original HB. To check on this point, the residue was diluted with OM-2 to a concentration corresponding to the original 40%w Core III A HB solution. The HHB content of this solution was determined: 2.8%w, whereas the original coolant contained 2.5%w HHB.

TABLE I

Percolation experiments on Attapulgus Clay

Expt. No.	A 229	A 57	A 87	A 268
Column	Glass	Stainless steel	Stainless steel	Stainless steel
Column diam. (cm)	1.2	4.0	4.0	4.0
Bed weight (g)	35	620	600	610
Temp. (^{o}C)	165	180	180	360
Feed rate (g/min)	2	53	47	54
Feed	30%w Core IIIA HB in OM-2	30%w Core IIIA HB in OM-2	Grenoble, 320^{o}C, Feed-and-Bleed Stock A, 23%w HB	30%w Core IIIA HB in OM-2
HHB content of feed (%w)	2.5	2.3	4.8	2.3
Fouling test of feed (mg/cm2)	-	3.4	2.6	4.0

Effluent / Absorbent (=E/A) (g/g)	HHB (%w)	E/A (g/g)	HHB (%w)	Fouling Test (mg/cm2)	E/A (g/g)	HHB (%w)	Fouling Test (mg/cm2)	E/A (g/g)	HHB (%w)	Fouling Test (mg/cm2)
0 - 1.3	1.7	0 - 0.9	1.4	3.0	0 - 0.7	3.5	2.7	0 - 0.3	2.1	-
1.3- 2.3	2.2	0.9-1.6	1.6	2.5	0.7-1.4	3.9	2.5	0.3-1.0	1.6	-
2.3- 3.3	-	1.6-2.4	-	2.4	1.4-2.1	4.0	2.8	1.0-2.0	1.7	2.8
3.3- 4.2	2.2	2.4-3.2	2.2	2.9	2.1-2.8	4.1	3.3	2.0-2.9	2.1	2.6
4.2- 5.6	-	3.2-4.0	2.1	2.6	2.8-3.5	4.3	2.8	2.9-3.8	2.1	2.4
5.6- 6.8	1.9	4.0-4.6	2.1	1.9	3.5-4.3	4.6	2.5	3.8-4.7	2.1	3.1
6.8- 7.9	2.2	4.6-5.4	1.8	-	4.3-5.1	4.0	2.1	4.7-5.6	2.4	-
7.9- 9.2	2.4	5.4-6.2	2.0	2.4	5.1-5.8	4.3	-	5.6-6.5	2.4	3.3
9.2-10.2	2.3	6.2-6.9	2.3	-	5.8-7.0	4.6	1.8	6.5-7.9	-	3.2
10.2-11.7	1.9				7.0-8.8	5.0	-			
11.7-12.8	-									
12.8-13.8	2.1									
13.8-15.2	-									
15.2-18.3	2.2									
18.3-19.9	2.3									
19.9-21.8	-									
21.8-22.8	2.7									

TABLE II

Percolation experiments on Attapulgus Clay in glass columns

Experiment	A 201	A 221	A 261	A 271
Temperature (^{o}C)	180	360	360	180
Column diam. (cm)	1.8	1.0	1.0	1.8
Bed weight (g)	39.5	17.8	16.0	41.2
Feed	40%w Core IIIA HB in OM-2 *)	40%w Core III A HB in OM-2	40%w Core III A HB in OM-2	40%w Core III A HB in OM-2
Feed rate (g/min)	-	7.6	5.7	13.0
Oxygen content of original coolant (ppm)	525	350	350	350

E/A (g/g)	Oxygen content (ppm)	E/A (g/g)	Oxyg. cont. (ppm)	E/A (g/g)	Oxyg. cont. (ppm)	E/A (g/g)	Oxyg. cont. (ppm)
0 - 3.1	145	0 - 10.7	200	0 - 2.8	285	0 - 6.3	200
3.1 - 9.4	250						
9.4 - 12.4	330						

*) Previously, during 6 hrs at 300^{0}C, air has been passed through.

TABLE III

Percolation experiment on Attapulgus Clay, A 276

Column	: Glass
Column diameter (cm)	: 1.2
Bed weight (g)	: 25
Temperature (^{o}C)	: 180
Feed rate (g/min)	: 7.1
Feed	: 40%w Core IIIA HB in OM-2
HHB content of feed (%w)	: 3.4
Oxygen content of feed (ppm):	1100

E/A (g/g)	HHB (%)	Oxygen content (ppm)
0 - 2.1	2.1	620
2.1 - 4.6	2.8	1050
4.6 - 7.2	3.4	1100
7.2 - 10.3	3.5	1300
10.3 - 12.6	3.4	1100

TABLE IV

Sorbed oxygen, total throughput with estimated errors from Table II and III

Run No.	E/A (g/g)	Oxygen cont. of orig. c. (ppm)	Total ox. throughput (mg/kg)	Oxygen cont. of treated c. (ppm)	Sorbed oxygen (mg/kg)
A201 fr. 1	3.1	525± 50	1630± 160	145± 50	1180± 320
A201 fr. 2	9.4	525± 50	4960± 470	250± 50	2940± 940
A201 fr. 3	12.4	525± 50	6530± 620	330± 50	3520±1440
A221	10.7	350± 50	3740± 530	200± 50	1600±1060
A261	2.8	350± 50	980± 140	285± 50	180± 280
A271	6.3	350± 50	2200± 310	200± 50	940± 620
A276 fr. 1	2.1	1100±100	2310± 210	620± 60	1010± 340
A276 fr. 2	4.6	1100±100	5060± 460	1050±100	1140± 840
A276 fr. 3	7.2	1100±100	7920± 720	1100±100	1140±1360
A276 fr. 4	10.3	1100±100	11330±1030	1300±100	530±1980
A276 fr. 5	12.6	1100±100	13860±1260	1100±100	530±2440

The difference between these two values can hardly be called significant and even if so, represents only a removal of sorbate of 0.1%w of the bed weight. From the HHB analyses of the various fractions (see Table I) it can be estimated that the quantity of HHB retained on the bed amounts to 4 to 6%w of Attapulgus Clay present.
This shows that HHB cannot be removed from the clay by simple elution techniques and it is concluded that the sorption process in the case of Attapulgus Clay in contact with polyphenyl coolants is irreversible.

Moreover, it is a well known fact (1) that Attapulgus Clay in contact with polyphenyl becomes readily covered with a black deposit. On elution with all kinds of aromatic solvents this black layer cannot be removed. The only way to restitute the original, yellowish-orange appearance is to burn off the adherent components at 500°-600°C, converting the substance into its combustion products. Thus also the formation of these black deposits is irreversible.

3.2. Retention Capacity

The above proved irreversibility of the sorption process procures a simple means of investigation of the sorptive capacity of Attapulgus Clay. The quantity of sorbate on the clay can be directly determined by a simple weighing technique. This technique involves drying the Attapulgus Clay to constant weight before use under standard conditions (10 cm Hg and 150°C), thorough elution and washing of the clay bed after a percolation run and subsequent drying of the spent clay to constant weight under the same standard conditions. The resulting increase in weight is the quantity of sorbate retained.

Elution is performed at working temperature by passing through the bed of pure OM-2 until the brown colour of the eluate has completely disappeared, which requires usually a quantity of 5 to 10 times of the bed's weight. Subsequent washing of the bed is done with xylene at 130° to 140°C until the solvent passes colourless and finally with 5 times the bed's weight of benzene or toluene to remove all xylene.

On this basis a number of determinations of the quantity of sorbate re-

tained on an Attapulgus bed have been carried out.

The variables in these experiments are: contact time, quantity of effluent, quantity of sorbent, HB concentration, HB composition and temperature.

Attaclay 24/28 A-LVM from the Minerals and Chemicals Philipps Corporation, sieve fraction 40-50 mesh has been used. Generally, no other pretreatment than the drying procedure has been applied (see also Ch. 4.3.). The majority of the experiments was carried out at 180°C in a glass column of an internal diameter of 18 mm.

The coolants used are: High Boilers, ex OMRE Core III A, in Gilotherm OM-2 (5%, 10%, 20%, 40%w), solutions of various fractions of a fractional distillation of Core III A HB *) and two coolants from feed-and-bleed experiments in the BLO-3 loop at Grenoble (France) of 5 and 23%w HB, respectively.

The experimental details of the experiments are given in Table V.

Without taking into consideration variations of the amounts of Attapulgus and coolant used, the results of the runs at coolant rates varying from 2400 to 4800 kg/h-m^2 can be represented as a family of curves plotting the percentage weight increase of Attapulgus against contact time. These curves, Figures 2 and 3, lead to the conclusions that:

a) In all cases the weight of deposits tends to reach a maximum value which may be called the saturation capacity.

b) The saturation capacity is independent on the impurity concentration (Fig. 2).

---

*) Pressure: 1 mm Hg; Fraction 1 (20% of feed) passes over at 230-330°C, Fraction 2 (33% of feed) at 330-360°C, Fraction 3 (13% of feed) at 360-370°C (top temperature).

TABLE V

Percolation experiments in glass columns: ϕ_i = 1.8 cm

Exp. No.	Bed weight (g)	Feed (g)	Feed rate (g/min)	Contact time*) (min)	W**) (%w)
	40% Core III A HB in OM-2				
271	41.16	260	13.0	20	2.8
053	48.62	335	11.2	30	3.9
043B	50.07	610	12.2	50	4.2
083	31.96	1400	15.4	91	4.5
	20% Core III A HB in OM-2				
032B	28.86	130	13.0	10	2.2
032A	27.98	298	13.0	23	3.1
153	51.23	54	1.6	33	1.5
123	80.73	295	9.5	31	2.4
113	112.45	325	10.8	30	2.3
163	24.37	1191	38.5	31	4.1
032C	28.19	626	13.2	47	4.3
162	36.55	875	14.8	59	4.7
043A	48.08	1135	15.1	75	4.6
	10% Core IIIA HB in OM-2				
033A	49.59	320	16	20	1.2
023	52.27	375	12.5	30	2.6
093B	52.62	849	15.6	55	3.1
033B	48.75	935	13.5	69	4.9
	5% Core IIIA HB in OM-2				
083B	60.05	465	18.6	25	1.8
252	51.59	900	15.5	58	1.3
093A	72.51	1380	15.2	91	3.1
262	50.96	2025	16.8	120	4.0
	Grenoble 320°C, Feed-and-Bleed, Stock B, 5%w HB				
214B	54.71	470	15.6	30	2.5
084	57.12	740	16.4	45	2.9
144	52.63	1000	18.2	55	3.7
244	95.74	800	13.3	60	3.2
094A	53.54	2035	19.7	103	4.6

(Table V - continued)

Exp. No.	Bed weight (g)	Feed (g)	Feed rate (g/min)	Contact time*) (min)	W**) (%w)
	Grenoble 320°C, Feed-and-Bleed, Stock A, 23%w HB				
204A	50.46	300	13.1	23	4.9
224B	50.46	400	11.8	34	4.7
204B	50.67	500	12.5	40	5.5
214A	46.12	950	15.6	61	5.2
224A	50.67	1330	14.6	91	6.3
	6%w Solution of Distillation Residue, dist. 22/2 in OM-2				
064B	55.47	277	18.5	15	3.5
054	54.09	525	15.9	33	5.1
074	56.40	525	13.5	39	5.8
064A	57.22	673	16.8	40	5.3
074B	57.10	1035	16.7	62	7.1
094B	54.55	1750	14.3	122	8.9
	25%w Solution of Fraction 1, dist. 22/2 in OM-2				
173	52.59	442	14.9	29	2.0
173B	52.35	638	10.4	61	1.9
	25%w Solution of Fraction 3, dist. 22/2 in OM-2				
223	53.19	350	9.4	37	1.9
233	52.50	500	6.7	75	4.6

*) By "Contact time" is meant the total time the clay bed is in contact with the feed.

**) W is the percentage weight increase of the clay bed, i.e. the weight of sorbate retained.

c) The saturation capacity is a function of the HB-origin (Fig. 3).

d) In the case of various concentrations of Core III A HB, at 5%w and 10%w the sorption rate is approximately proportional to the concentration, whereas the runs at 20%w and 40%w do not show any influence of concentration (Fig. 2).

Conclusion d) implies that there must be a concentration limit above which the sorption rate is no longer a function of the impurity concentration.

From material balances over several runs (Table I) it appears that the total weight of HHB retained equals approximately the weighed increase of the deposits, so that the final conclusion is that these impurities are retained on the clay by chemisorption.

The evidence in favour of chemisorption is principally sustained by the facts that

- the process is irreversible,
- the saturation capacity is independent on concentration.

4. SATURATION CAPACITY

4.1. Effect of HB-origin

The actual values for the saturation capacity can be obtained from a plot of the data as W against 1/t (Fig. 4). The values for the saturation capacity obtained in these series lie all between 5 and 10%w.

It has already been concluded that these values are not affected by the HB-concentration, but vary with various HB-origins. The general trend is that the saturation capacity increases with increasing mean molecular weight of the HB, see Table VI.

TABLE VI

Saturation capacity of Attapulgus Clay at 180°C

High-Boilers	M_n	Conc. (%w)	Sat. Cap. (%w)
Core III A	500	40	5
Core III A	500	20	5
Grenoble, 320°C Feed-and-Bleed, Stock B	600	5	6
Grenoble, 320°C Feed-and-Bleed, Stock A	650	23	7
Distillation Residue of Core III A HB	1000	6	10

4.2. Effect of temperature

The working temperature for the percolation runs described before has been selected at 180°C mainly for practical purposes.

Haroldsen and Florence (2) state that the bed performance improves with increasing temperatures to 400°C. However, it must be noted that the original evidence in favour of this statement is not very convincing.

The effect of elevated temperatures on the saturation capacity has been investigated by recirculation of about 2 kg of 30%w Core III A HB in OM-2 for at least 6 h over a small Attapulgus column containing approximately 40 g of clay.
At the end of the run the percentage weight increase of the clay has been determined in the usual way. The results are given in Table VII. It follows that the saturation capacity is hardly affected by temperature in the range of 180-360°C.

Additionally, it is noted that between comparable runs at 180°C and at 360°C in stainless steel columns no significant difference can be demon-

strated, neither in the results of the fouling tests, nor in the HHB content of the fractions (Table I).

TABLE VII

Effect of temperature on the saturation capacity for 30%w Core III A HB in OM-2

Temperature (°C)	Saturation Capacity (%w)
180	5.1
235	5.7
250	5.5
290	4.5
360	5.4

4.3. Effect of pretreatment

All previous percolation runs have been carried out with Attapulgus Clay, preliminary dried at 150°C in vacuum.
Preceding thermal activation enhances the performance of the clay to a certain extent (1). Optimal pretreatment should consist of heating the clay to 400°C for a prolonged period.

The effect of pretreatment of the clay has been investigated by carrying out a few percolation runs with activated Attapulgus Clay.
The results are represented in Table VIII.

The use of pretreated clay gives a marked increase in the saturation capacity by approximately 50%.

The data from Table VIII together with those for Grenoble Feed-and-Bleed Stock A (saturation capacity 7%w) are given in Fig. 5.
It follows that the rate of formation of the deposits does not deviate considerably from other runs where the saturation capacity is also approximately 7%w.

TABLE VIII

Percolation experiments with Attapulgus Clay, pretreated at 400°C for 5 h. Feed: 30%w Core III A HB in OM-2. Temp.: 180°C.

Expt. No.	Bed Weight (g)	Feed (g)	Feed Rate (g/min)	Contact Time (min)	W (%w)
A 1903	27.60	166	10.4	16	3.7
A 1803	24.39	289	9.3	31	4.6
A 2706	24.64	331	7.1	48	5.4
A 2010	25.20	1985	15.8	180	7.3

5. RETENTION MECHANISM

5.1. General considerations

When chemisorption phenomena on an active surface are encountered, the transfer of the compound in question from the bulk of the liquid to the active spot proceeds according to the following mechanism:

- diffusion of the molecule from the bulk to the surface,
- physical adsorption of the molecule on the active spot,
- reaction of the molecule and (eventually) occupation of the active spot by the molecule and/or its reaction products.

The rate equations for these steps are

$$\text{Diffusion: } N_D = K'_L S(C-C_i) \quad (1)$$

$$\text{Adsorption: } N_A = K'_A SC_i q_v - K'_D S q_A \quad (2)$$

with: N_D the rate of diffusion *),
K'_L the mass transfer coefficient,
S the specific surface of the solid,
C the concentration of the solute in the bulk of the liquid,
C_i the concentration at the interface,
N_A the net rate of adsorption,
K'_A the mass transfer coefficient for adsorption,
K'_D the mass transfer coefficient for desorption,
q_v the fraction of the active sites being vacant,

*) Any consistent system of dimensions can be used.

q_A the fraction of the active sites, occupied solely by adsorption.

For the reaction step evidently no general rate equation can be given; this equation depends completely on the type of surface reaction in question.

In the present case it is most likely that the reaction takes place on the active sites only. Once having reacted, the site is considered to be occupied definitively and furthermore inactive.

The reaction rate can thus be represented by:

$$N_R = K'_R S q_A \qquad (3)$$

with: N_R the reaction rate,

K'_R the reaction rate constant.

When the process is at steady state:

$$N_D = N_A = N_R = \frac{dw}{dt} \qquad (4)$$

with: w the local weight increase on Attapulgus,

t the contact time.

A mass balance over the number of active sites gives:

$$q_A + q_v + \frac{1}{\Upsilon S}\int N_R = 1 \qquad (5)$$

where Υ is the maximum mass of reaction products per unit specific surface.

The saturation capacity Q is equal to ΥS and by definition $\int_o^t N = w$.
Substitution of these relations into Eq. 5 yields:

$$q_A + q_v + \frac{w}{Q} = 1 \qquad (6)$$

Substitution into Eq. 2 of:

$$C_i = C - \frac{dw/dt}{K_L} \qquad (1)$$

$$q_A = \frac{dw/dt}{K_R} \qquad (3)$$

$$q_v = 1 - q_A - \frac{w}{Q} \qquad (6)$$

$K_A = K'_A S$ ..... etc.

yields after some rearrangement the general equation:

$$\left(C - \frac{dw}{K_L dt}\right)\left\{\frac{dw}{K_R dt} - \left(1 - \frac{w}{Q}\right)\right\} + \frac{dw}{dt}\left(\frac{1}{K_A} + \frac{K_D}{K_A K_R}\right) = 0 \qquad (7)$$

The boundary conditions for this differential equation are:

$t = 0,\ w = 0$

$t = \infty,\ \frac{dw}{dt} = 0,\ w = Q$

From the second boundary condition it follows that Q is independent on the impurity concentration C, which is in accordance with the observations made in Ch. 3.2., (page 11 , conclusion b).

Eq. 7 can be solved by ordinary mathematic techniques yielding as general solution for the system:

$$\left(\frac{2CK_L}{Q}\right)t = (1-z) + \sqrt{Z_o} - \sqrt{Z} + (a-c)\ln\frac{\sqrt{Z_o} + 1 + (a-c)}{\sqrt{Z} + z + (a-c)} - (a+c)\ln\frac{\left[\sqrt{Z_o} + (a+c) + \frac{a-c}{a+c}\right]z^2}{\sqrt{Z} + (a+c) + \frac{a-c}{a+c}z} \qquad (8)$$

where: $z = 1 - w/Q$

$a = K_L/K_A(1+K_D/K_R)$

$c = K_L C/K_R$

$Z = (a+c)^2 + 2(a-c)\,z + z^2$

$Z_o = (a+c)^2 + 2(a-c) + 1$

The general solution given in Eq. 8, although fully representative for the system, appears to be complicated for practical application. A closer investigation of Eq. 7 provides additional information.

Each step of the overall sorption process (diffusion, adsorption and reaction) offers a certain resistance to the mass transfer. It is improbable that all three resistances are of the same order of magnitude.
The consequences of one resistance being negligible in comparison with the other two, are:

1) Resistance to diffusion is negligible : $1/K_L \longrightarrow 0$,
2) Resistance to reaction is negligible : $1/K_R \longrightarrow 0$,
3) Resistance to adsorption is negligible : $1/K_A \longrightarrow 0$.

The general equation (Eq. 7) has been solved for dw/dt (=w') in the three above mentioned hypothetical cases. The solutions are given in Table IX.

It appears that in the first two cases, w' is always a function of or proportional to the liquid bulk concentration C.
When the resistance due to adsorption is negligible, two solutions for w' are obtained, of which generally only one can be right for a fixed condition.

The general equation in this case is transferred into:

$$\left(C - \frac{w'}{K_L}\right)\left[\frac{w'}{K_R} - (1-w/Q)\right] = 0 \qquad (9)$$

The various conditions are:

A) $K_L C < K_R(1-w/Q)$

B) $K_L C > K_R(1-w/Q)$

C) $K_L C = K_R(1-w/Q)$

Condition A:

$$K_L C < K_R(1-w/Q) \text{ or} \qquad (10)$$
$$K_L C + K_L \Delta = K_R(1-w/Q)$$

Substitution of Eq. 10 into Eq. 9 gives:

$$(K_L C - w')(w' - K_L C - K_L \Delta) = 0$$

The solutions become:

$$w'_1 = K_L C$$

$$w'_2 = K_L(C + \Delta)$$

Eq. 1 states

$$w' = K_L(C-C_i), \text{ where } C_i \geq 0$$

This implies that in this case w'_2 is a false solution and

$$\frac{dw}{dt} = K_L C \qquad (11)$$

Condition B:

$$K_L C > K_R (1 - w/Q) \therefore \qquad (12)$$

$$K_L C = K_R (1 - w/Q) + K_R \Delta$$

Substitution of Eq. 12 into Eq. 9 gives:

$$\left[K_R (1 - w/Q) + K_R \Delta - w' \right] \left[w' - K_R (1 - w/Q) \right] = 0$$

The solutions become:

$$w'_1 = K_R (1 - w/Q + \Delta)$$

$$w'_2 = K_R (1 - w/Q)$$

From Eq. 3 and Eq. 4 follows:

$$w' = K_R q_A = K_R (1 - w/Q - q_v), \text{ where } q_v \geq 0$$

This implies that in this case w'_1 is a false solution and

$$\frac{dw}{dt} = K_R (1 - w/Q) \qquad (13)$$

Condition C:

$$K_L C = K_R (1 - w/Q)$$

Both terms of Eq. 9 are equal to zero and thus

$$\frac{dw}{dt} = K_L C = K_R (1 - w/Q)$$

From experimental evidence it has already been concluded that there is a concentration limit above which the sorption rate is no longer a function of impurity concentration. (Chapter 3.2., page 14 , conclusion d).

The hypothetical case in which resistance due to adsorption is negligible, perfectly fits to this conclusion.
It seems therefore justified to neglect in the present case the resistance due to adsorption and to adopt the model represented by Eq. 9 for the sorption mechanism.

The case in which $K_L C < K_R (1 - w/Q)$ so that

$$\frac{dw}{dt} = K_L C$$

TABLE IX

VARIOUS SOLUTIONS FOR Eq. 7:

$$\left(C-\frac{w'}{K_L}\right)\left\{\frac{w'}{K_R}-\left(1-\frac{w}{Q}\right)\right\}-w'\left(\frac{1}{K_A}+\frac{K_D}{K_A K_R}\right)=0$$

Negligible resistance due to:	Equation 7 becomes	Solution
Diffusion : $1/K_L = 0$	$C\left[\frac{w'}{K_R}-\left(1-\frac{w}{Q}\right)\right]-w'\left[\frac{1}{K_A}+\frac{K_D}{K_R K_A}\right]=0$	$w'=\frac{C(1-w/Q)K_R K_A}{CK_A-K_R-K_D}$
Reaction : $1/K_R = 0$	$\left(C-\frac{w'}{K_L}\right)\left[-\left(\frac{1-w}{Q}\right)\right]-w'\left[\frac{1}{K_A}+\frac{K_D}{K_R K_A}\right]=0$	$w'=\frac{C(1-w/Q)K_L K_R K_A}{K_A K_R(1-w/Q)-K_L K_R-K_D K_L}$
Adsorption : $1/K_A = 0$	$\left(C-\frac{w'}{K_L}\right)\left[\frac{w'}{K_R}-(1-w/Q)\right]=0$	$w'_1 = K_L C$ $w'_2 = K_R(1-w/Q)$

will be called: "diffusion controlled", whereas the other case:

$K_L C > K_R (1 - w/Q)$ so that

$$\frac{dw}{dt} = K_R (1 - w/Q)$$

will be referred to as "reaction controlled".

5.2. Material Balance Relations

The conservation equation for an infinitesimal thickness of bed, expresses the fact that any loss of sorbate from the solution flowing through the section must equal the gain of sorbate on the solid at that section:

$$-LdC = S_B \rho_B dX \frac{dw}{dt} \tag{14}$$

where L the liquid rate,

S_B the cross sectional area of the column,

ρ_B the density of bed,

X the bed height,

C the sorbate concentration.

In the reaction controlled case:

$$\frac{dw}{dt} = K_R(1-w/Q)$$

which can be transformed into

$$\frac{dw}{dt} = K_R \exp(-K_R t/Q) \tag{15}$$

Substitution of Eq. 15 into Eq. 14 and integration yields:

$$\int_X^0 dC = -\frac{S_B \rho_B}{L} K_R \exp(-K_R t/Q) \int_X^0 dX$$

which gives

$$C_X = C_o - \frac{XS_B \rho_B}{L} K_R \exp(-K_R t/Q) \tag{16}$$

If the value of C_X decreases to such an extent that

$$C_X \leq \frac{K_R}{K_L}(1-w/Q) = (K_R/K_L) \exp(-K_R t/Q)$$

the sorption rate is no longer reaction controlled but given by Eq. 11: $dw/dt = K_L C$.

At the transition point

$$\frac{dw}{dt} = K_L C_X = K_R \exp(-K_R t/Q)$$

which gives:

$$K_L \left[C_o - \frac{XS_B \rho_B}{L} K_R \exp(-K_R t/Q) \right] = K_R \exp(-K_R t/Q)$$

from which follows:

$$X_t = \frac{L}{K_L S_B \rho_B} \left[\frac{K_L C_o}{K_R} \exp(+K_R t/Q) - 1 \right] \qquad (17)$$

For the diffusion controlled part, when

$$C < (K_R/K_L) \exp(-K_R t/Q)$$

Eq. 14 becomes:

$$-L dC = S_B \rho_B \, dX \, K_L C. \qquad (18)$$

Integration of dC from 0 to X gives:

$$\frac{C_X}{C_o} = \exp\left(-\frac{XS_B \rho_B}{L} \cdot K_L\right) \qquad (19)$$

If the process, in the upstream part of the bed, is reaction controlled, followed by a downstream diffusion controlled part, the exit sorbate concentration can be found by consideration of the fact that at the transition point X_t:

$$C_t = (K_R/K_L) \exp(-K_R t/Q)$$

Downstream the transition point

$$\frac{C_X}{C_t} = \exp\left(-\frac{(X-X_t)S_B \rho_B}{L} \cdot K_L\right)$$
$$= \exp(XS_B \rho_B - X_t S_B \rho_B) \frac{K_L}{L} \qquad (20)$$

Introduction of expressions for C_t and X_t (Eq. 17) yields:

$$C_X = \frac{K_R}{K_L} \exp(-K_R t/Q) \exp(-P) \quad \text{where}$$

$$P = \frac{K_L}{L} \left(XS_B \rho_B - \frac{L}{K_L} \left[\frac{K_L C_o}{K_R} \exp(+K_R t/Q) - 1 \right] \right)$$

Introducing $XS_B \rho_B = A$ (the weight of sorbent in the bed) and rearrangement gives:

$$C_X = \frac{K_R}{K_L} \exp\left[\frac{K_L C_o}{K_R} \exp\left(\frac{K_R t}{Q}\right) - \left(\frac{K_R t}{Q} + \frac{AK_L}{L} + 1\right)\right] \qquad (21)$$

The three, above derived, equations for C_X are summarized in Table X together with the preconditions for each case.

At present, expressions for the total weight increase of the bed, can be derived from

$$L\int_0^t (C_o - C_X)dt = A\int_0^t dw = AW$$

The so obtained expressions are given in Table XI.

It has to be noted that the equations of Table XI represent the relative weight increase of the bed as a function of contact time t, when all feed has been passed through. This equals the actual condition when a run is completed by subsequent washing with pure terphenyl.

Consequently the equations do not represent the relative weight increase of the column at a certain intermediate point of time τ. In the latter case, for development of the equations another parameter for contact time should have been chosen, taking care of the fact that at a distance x downstream the column, contact time t equals $\tau - x/V$, where V stands for the linear feed velocity.

TABLE X

EXPRESSIONS FOR THE EXIT IMPURITY CONCENTRATION.

Condition	Case	C_x
$C_o > C_x \geq \frac{K_R}{K_L} \exp\left(-\frac{K_R t}{Q}\right)$	Reaction controlled	$C_x = C_o - \frac{AK_R}{L} \exp\left(-\frac{K_R t}{Q}\right)$
$C_o \geq \frac{K_R}{K_L} \exp\left(-\frac{K_R t}{Q}\right) \geq C_x$	Partly reaction controlled Partly diffusion controlled	$C_x = \frac{K_R}{K_L} \exp\left[\frac{K_L C_o}{K_R} \exp\left(\frac{K_R t}{Q}\right) - \left(\frac{K_R t}{Q} + \frac{AK_L}{L} + 1\right)\right]$
$C_o \leq \frac{K_R}{K_L} \exp\left(-\frac{K_R t}{Q}\right)$	Diffusion controlled	$C_x = C_o \exp\left(-\frac{AK_L}{L}\right)$

TABLE XI

EXPRESSIONS FOR SORBATE CONCENTRATION ON THE SORBENT INTEGRATED OVER THE BED.

Reaction controlled	$W = Q\left(1 - \exp\frac{-K_R t}{Q}\right) \quad \therefore \quad 1 - \frac{W}{Q} = \exp\left(\frac{-K_R t}{Q}\right)$ (Eq 22)
Partly reaction, partly diffusion controlled	$W = \frac{LC_o}{A}\left\{t - \frac{Q}{K_R}\exp\left(-\frac{AK_L}{L} - 1\right)\left[-\frac{K_R}{K_L C_o}\exp\left[\frac{K_L C_o}{K_R}\exp\left(\frac{K_R t}{Q}\right) - \frac{K_R t}{Q}\right] + \right.\right.$ $+\frac{K_R t}{Q} + \ln\frac{K_L C_o}{K_R} + \exp\left[\frac{K_L C_o}{K_R}\exp\frac{K_R t}{Q}\right] +$ $\left.\left. + \frac{\exp\left[2\frac{K_L C_o}{K_R}\exp\frac{K_R t}{Q}\right]}{2.2!} + \frac{\exp 3\left(\frac{K_L C_o}{K_R}\exp\frac{K_R t}{Q}\right)}{3.3!} + \cdots \text{etc}\right]\right\}$ (Eq23)
Diffusion controlled	$W = \frac{LtC_o}{A}\left(1 - \exp\left(\frac{-AK_L}{L}\right)\right)$ (Eq24)

6. DETERMINATION OF RATE CONSTANTS

6.1. Determination of K_R

In the previous section it has been shown that the sorption process can be fully described in terms of feed rate, clay content of the column, saturation capacity, solute (= impurity) concentration, a reaction and a diffusion rate constant.

It is of interest to obtain numerical values for the two rate constants, as well as for the impurity concentration.

For the completely reaction controlled case, K_R can be obtained from the data from Table V. In this case a semilogarithmical plot of $1 - W/Q$ against t/Q should yield a straight line with a slope of $- K_R$ (Eq. 22, Table XI).

The above procedure has been carried out for the experiments with 40%w and 20%w Core III A HB in OM-2, 6%w Distillation Residue of Core III A HB in OM-2 and Grenoble 320°C Feed- and-Bleed, Stock A, 23%w HB. For the respective saturation capacities the values from Table VI have been adopted.

The results are represented in Fig. 6. From the combined experimental data it appears that K_R is apparently independent on Q. The numerical value obtained for K_R is 2×10^{-3} min^{-1}

6.2. Determination of K_L

The diffusion controlled case is more complicated than the reaction controlled one since in the rate equation (Eq. 24, Table XI) the impurity concentration as well as the diffusion rate constant are present. Both have to be considered as unknown quantities.

This difficulty is overcome by carrying out an experiment in which the clay bed consists of several, approximately identical, small columns in series. In this case for the n-th column:

$$W_n = (C_o)_n \frac{tL}{A_n} \left[1 - \exp - \left(\frac{A_n K_L}{L} \right) \right] \qquad \text{(see 27)}$$

Additionally

$$(C_o)_n = (C_x)_{n-1} \text{ and}$$

$$(C_x)_{n-1} = (C_o)_{n-1} \exp -\left(\frac{A_{(n-1)} K_L}{L}\right) \qquad \text{(from 19)}$$

From the above follows

$$W_n = \frac{tL}{A_n}\left[1 - \exp\left(-A_n K_L/L\right)\right](C_o)_o \exp(-Y) \text{ where}$$

$$Y = K_L/L\left\{A_{(n-1)} + A_{(n-2)} + A_{(n-3)} \ldots + A_o\right\}$$

$$W_n = \frac{C_o tL}{A_n}\left[1 - \exp -\left(\frac{A_n K_L}{L}\right)\right] \exp -\left[\frac{K_L}{L} \sum A_{o \ldots n}\right] \qquad (25)$$

Each column in the series contains about the same weight of Attapulgus Clay, so that $A_o \cong A_1 \cong A_2 \cong \ldots A_n$.

This means that:

$$\frac{C_o tL}{A_n}\left[1 - \exp -\left(\frac{A_n K_L}{L}\right)\right]$$

is a constant and Eq. 25 can be modified into:

$$W_n = P \exp\left(-\frac{K_L}{L} \sum A_{o \ldots n}\right) \qquad (26)$$

A semilogarithmical plot of W_n against $\Sigma A_{o \ldots n}$ will yield a straight line with a slope $- K_L/L$.

The experiment has been carried out by passing a coolant with low impurity concentration (Grenoble 320°C Feed-and-Bleed, Stock B, 5%w HB) in upflow through five small columns in series. Experimental data are given in Table XII and in Fig. 7. It follows that at 180°C, $K_L = 0.25 \text{ min}^{-1}$.

TABLE XII

Experiment No. 24/4

Temp. (^{o}C)	:	180
Coolant	:	Grenoble 320^{o}C, Feed-and-Bleed, Stock B, 5%w HB
Contact time (min)	:	60
Feed (g)	:	800
Column diameter (mm)	:	12.5

Column	Weight (g)	Deposits (g)	W (%)
1	19.13	0.29	1.5
2	18.64	0.39	2.1
3	19.27	0.56	2.9
4	19.48	0.86	4.4
5	19.22	0.99	5.2

7. ESTIMATION OF IMPURITY CONCENTRATION

Once the value for K_L known, numerical values for the impurity concentration have been calculated from the data of Table V, for the experiments with 5%w, 10%w, 20%w Core III A HB in OM-2, Grenoble 320^{o}C Feed-and-Bleed, Stock B and the runs with 25%w distillation fractions of Core III A HB in OM-2. The results are given in Table XIII.

It is concluded that a substantial part of the HB is active on Attapulgus Clay.

For the fractional percolation runs carried out in the 4 cm internal diameter, stainless steel column at 180^{o}C HHB content determinations of the feed and of the various fractions have been performed (Table I).

By simple substraction, the amount of HHB removed from the coolant can

be found. This should be representative for the term $C_o - C_x$, as expressed by the equations 16, 19 and 21. For the experiments carried out at 180°C, practically all other variables are known, so that for each run $C_o - C_x$ can also be calculated theoretically.

It appears that Run A 57 as well as Run A 87 are initially partly reaction, partly diffusion controlled; in this case C_x is calculated from Eq. 21.

Afterwards the process becomes fully reaction controlled and C_x can be found from Eq. 16.

The time (t^*) at which the transition takes place is found from the relation:

$$\frac{AK_L}{L} = \frac{K_L C_o}{K_R} \exp\left(\frac{K_R t^*}{Q}\right) - 1$$

which is a modification of Eq. 17.

For the runs carried out at 180°C, the theoretical lines together with the experimental points are shown in Fig. 8.
In general, taking into account the reproducibility of the HHB analysis (about 0.2%w) the experimental and theoretical results correspond reasonably.

TABLE XIII

Calculated Impurity Concentration

	Impurity concentration	
	With respect to total coolant (%w)	With respect to HB (%w)
Core III A HB 5%w in OM-2	0.2 ± 0.2	4
Core III A HB 10%w in OM-2	0.4 ± 0.2	4
Core III A HB 20%w in OM-2	0.9 ± 0.5	4
Grenoble 320°C, Feed-and-Bleed, Stock B, 5%w HB	0.4 ± 0.2	8
Distillation fractions of Core III A HB 22/2 Fraction 1 25%w HB	0.3 ± 0.1	1
22/2 Fraction 3 25%w HB	0.4 ± 0.2	2

8. CONCLUSIONS

In the present study it has been shown that the action of Attapulgus Clay in the presence of polyphenyl coolants consists of irreversible chemisorption of at least partly oxygenated impurities from the HHB range of the coolant.

The concentration of these impurities is 1 - 2%w for coolants containing about 30%w HB.

The saturation capacity of Attapulgus Clay is generally limited to approximately 5 - 10%w.

It is of interest to consider the consequences of the above data for the application of Attapulgus systems in large-scale reactor circuits.

The rate of formation of the sorbed impurities may be estimated by consideration of the quantity of organic bound oxygen introduced into the reactor

with the make up.

Virginal OM-2 used as make up coolant contains about 300 ppm organic bound oxygen. Thus, to a reactor containing 200 tons of coolant, operating at a make up rate of 100 kg/h, a steady introduction of 0.03 kg/h of bound oxygen takes place.
The oxygen content of the compounds will be 3 - 5%w (Chapter 2.1.).

The rate of formation of the "active impurities" can thus be estimated at 1 kg/h.

Use of Attapulgus Clay columns for the removal of these quantities yields a clay consumption of about 20 kg/h, which implies either the use of very large columns or the application of very short stand times for every column.

The above considerations make it very doubtful whether Attapulgus sorption systems can be effectively operated in an economical way in full scale reactor systems.

NOTATION

All dimensions are given in terms of weight (w), time (t) and length (l).

A	:	total weight of sorbent	(w)
C	:	liquid bulk concentration	$(-)$
C_i	:	ibid., at interface	$(-)$
C_o	:	ibid., initial	$(-)$
C_x	:	ibid., at bed height X	$(-)$
K_A	:	adsorption rate constant	(t^{-1})
K'_A	:	ibid.	$(w.l^{-2}.t^{-1})$
K_D	:	desorption rate constant	(t^{-1})
K'_D	:	ibid.	$(w.l^{-2}.t^{-1})$
K_L	:	diffusion rate constant	(t^{-1})
K'_L	:	ibid.	$(w.l^{-2}.t^{-1})$
K_R	:	reaction rate constant	(t^{-1})
K'_R	:	ibid.	$(w.l^{-2}.t^{-1})$
L	:	liquid flow rate	$(w.t^{-1})$
M_n	:	average number molecular weight	$(-)$
N_A	:	adsorption rate	(t^{-1})
N_D	:	diffusion rate	(t^{-1})
N_R	:	reaction rate	(t^{-1})
P	:	constant	
Q	:	saturation capacity	$(-)$
q_A	:	fraction of active sites occupied by adsorption	$(-)$
q_v	:	fraction of active sites vacant	$(-)$
S	:	specific surface	$(l^2.w^{-1})$
S_B	:	cross-sectional area of column	(l^2)
t	:	time	(t)
V	:	linear velocity	$(l.t^{-1})$
w	:	sorbate concentration on sorbent	$(-)$
W	:	ibid., integrated over bed weight	$(-)$
w'	:	sorption rate (= dw/dt)	(t^{-1})
X	:	bed height	(l)
$\triangle$	:	absolute value of a constant	

ρ_B	:	density of the bed	$(w.l^{-3})$
γ	:	maximum mass of reaction products per unit specific surface	$(w.l^{-2})$
τ	:	time parameter	(t)

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APPENDIX

DETERMINATION OF HHB-CONTENT BY PRECIPITATION

a) Method of operation

- About 1 g of coolant is weighed into a 100 ml beaker and heated to fusion at 120°C on a heating plate.
- 50 ml solvent (dodecane) is added under stirring, the solution is brought to the boil and kept boiling for approximately 1 minute.
- The solution is cooled down to room temperature upon which precipitation of the HHB takes place.
- Filtration over a G-4 glass filter crucible (pore diameter 6-7 μ) provided with a small layer of filter aid, previously dried to constant weight.
- Washing the filter cake and the beaker with 50 ml dodecane, followed by 100 ml heptane.
- Drying to constant weight at 130°C and a pressure of 20 mm Hg of both beaker and glass filter *).
- All analyses have to be duplicated.

b) Reproducibility and choice of solvent

The method has originally been developed with n-decane as a solvent, but for economical reasons it is now standardized for the use of n-dodecane. Dodecane is of nuclear quality, 99%, manufactured and sold by Progil, Paris.

Results obtained with dodecane are somewhat higher than those with decane. For a sample from a Grenoble BLO-4 Feed-and-Bleed, Stock,C2-42-320, No. 78, it has been found:

Solvent	Result
Decane	8.4% HHB
Dodecane	8.9% HHB

In the present report all HHB-analyses have been carried out with decane. From about 20 analyses of the same sample executed by 3 analists, the standard deviation for one determination has been calculated as 0.29%, which yield as reproducibility for the standard method: 0.2%w.

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*) Note: Both beaker and filter have to be weighed as the HHB often adheres to the beaker wall and cannot be quantitatively removed.

FIGURE 1

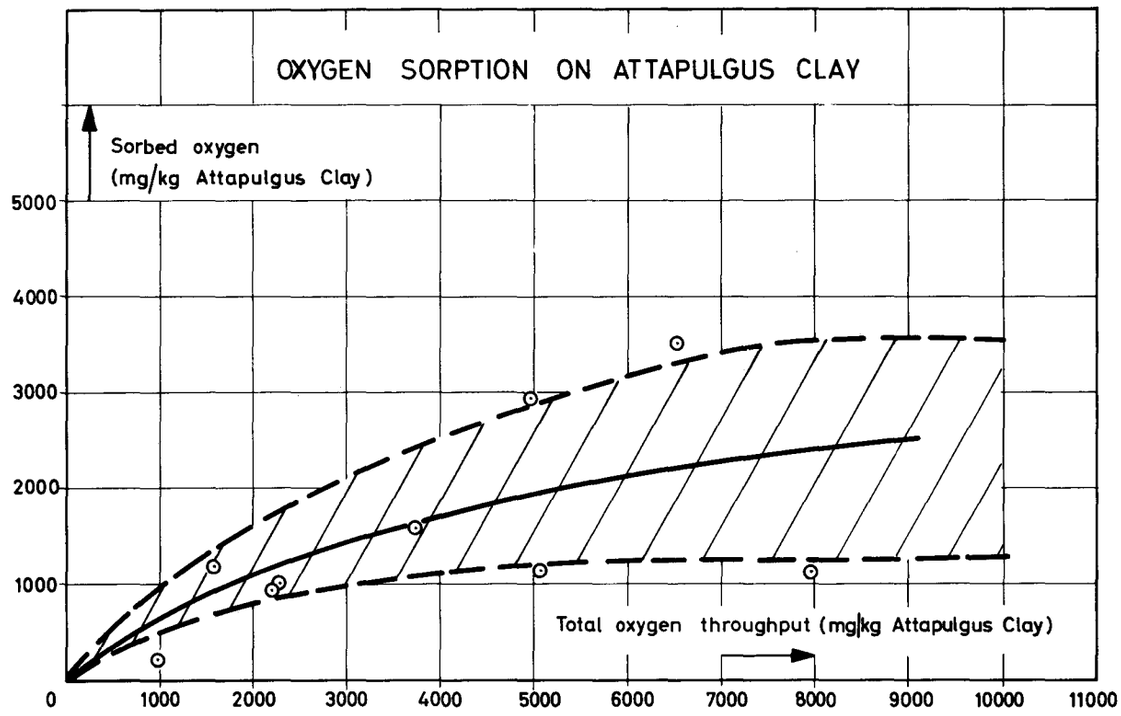
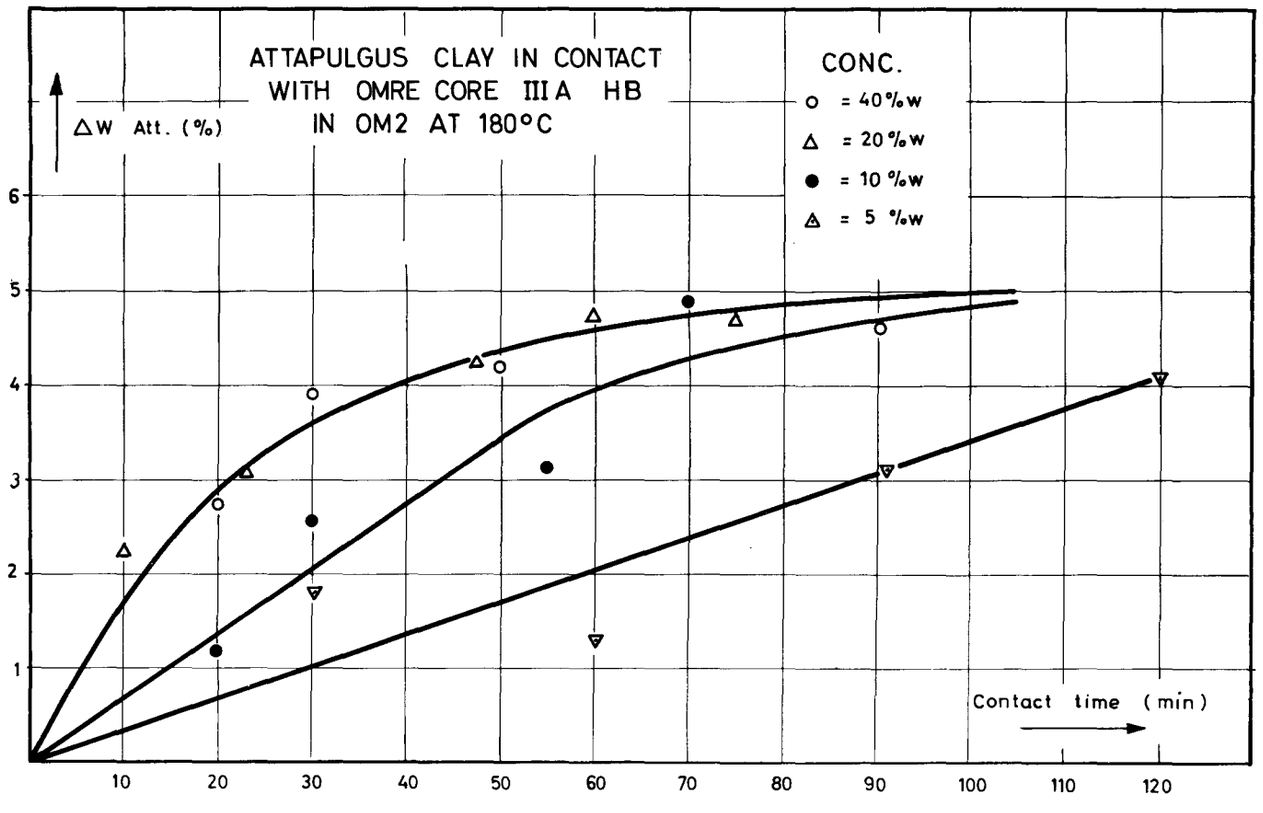


FIGURE 2



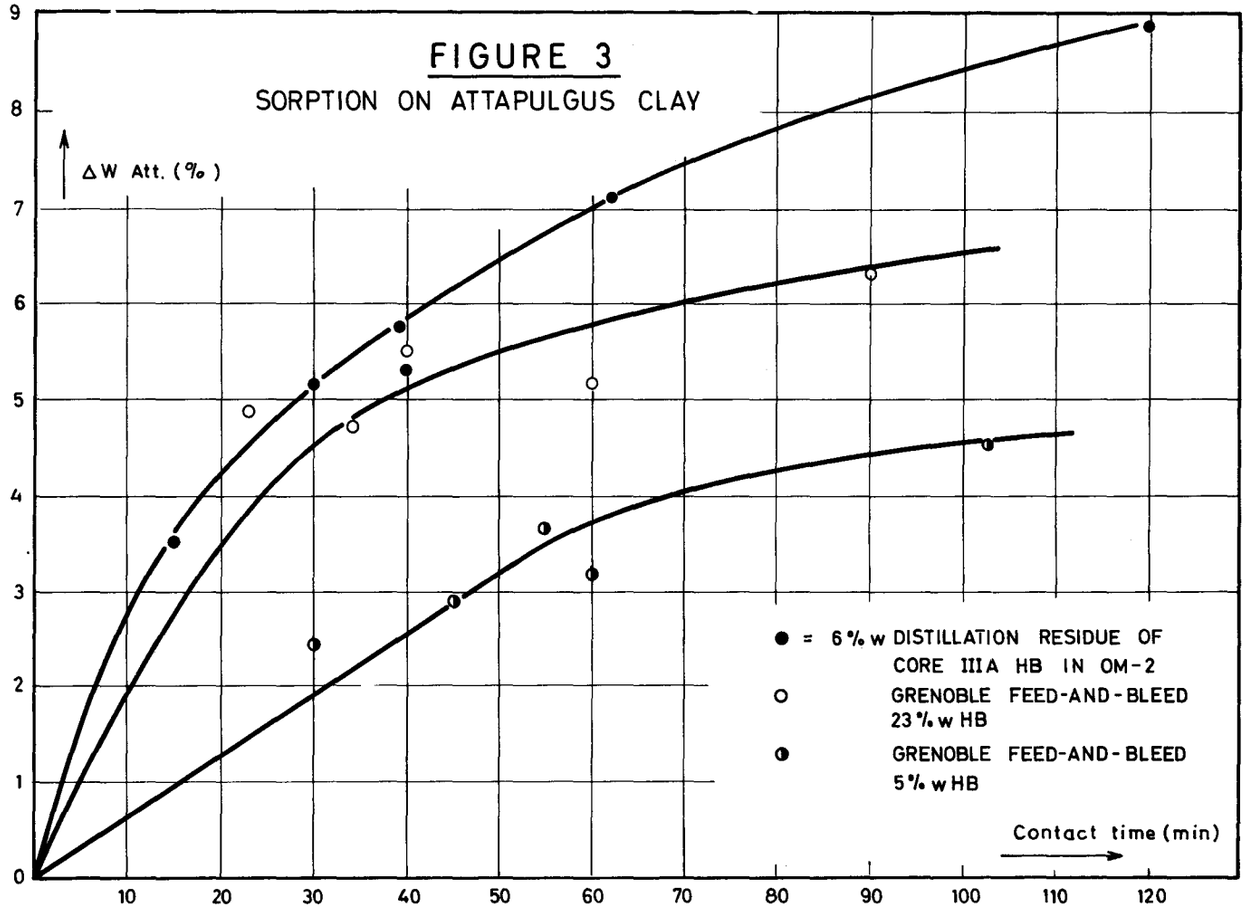


FIGURE 4

ESTIMATION OF SATURATION CAPACITY

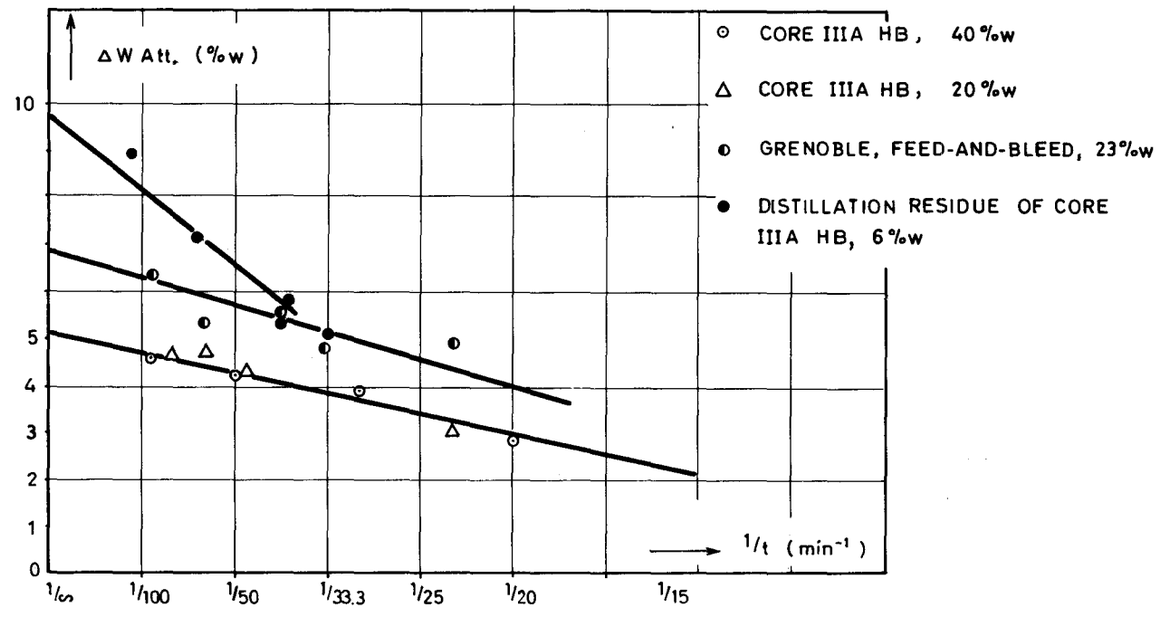


FIGURE 5

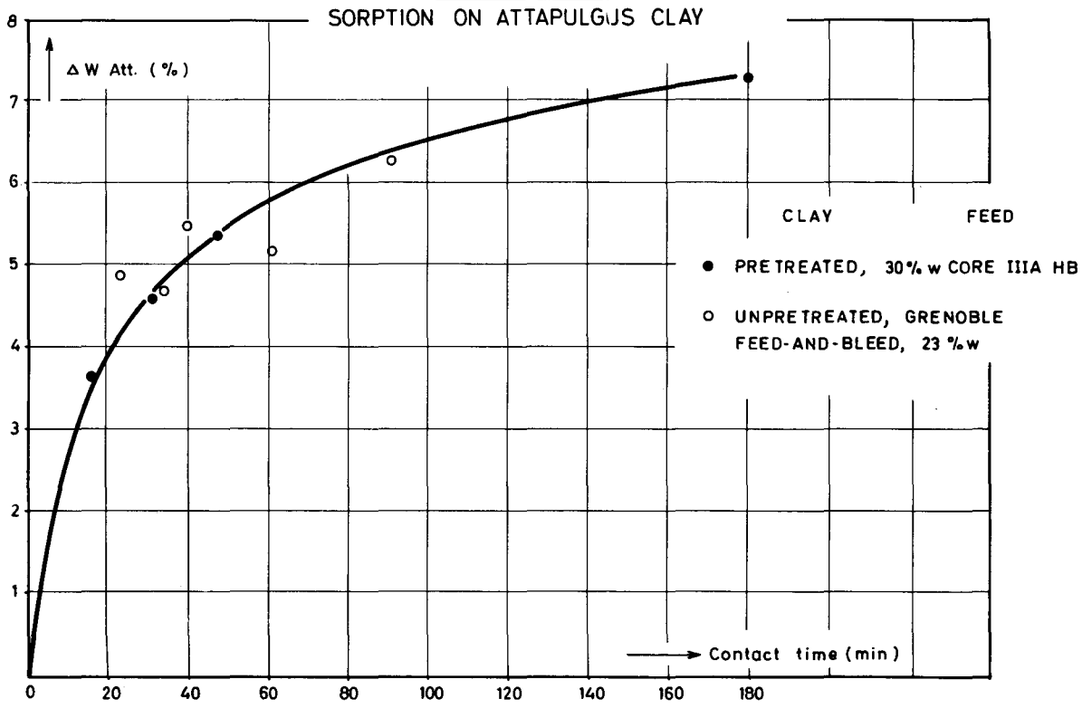


FIGURE 6

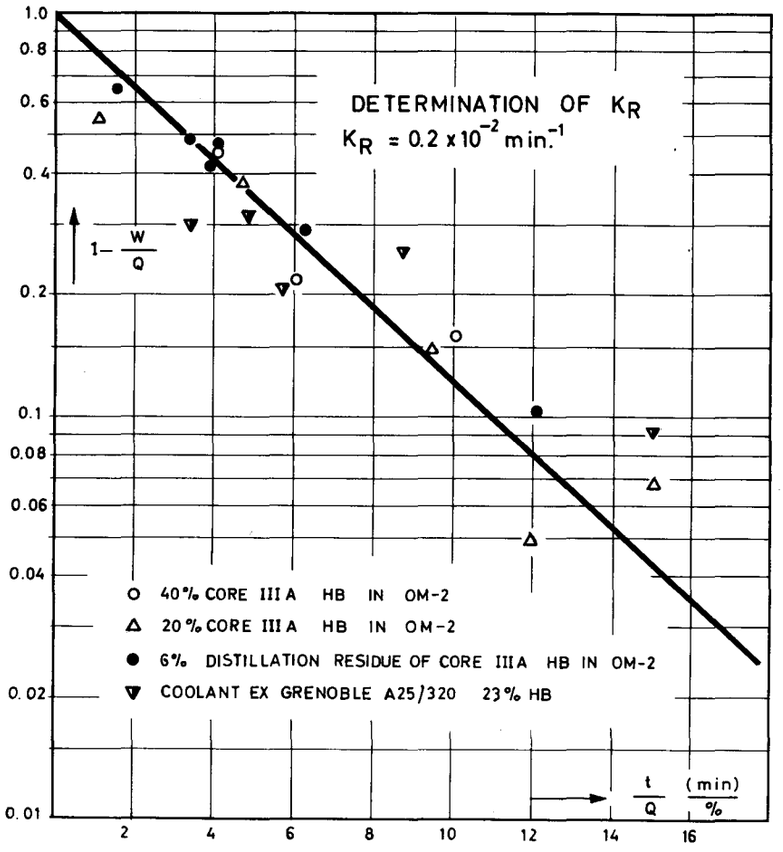
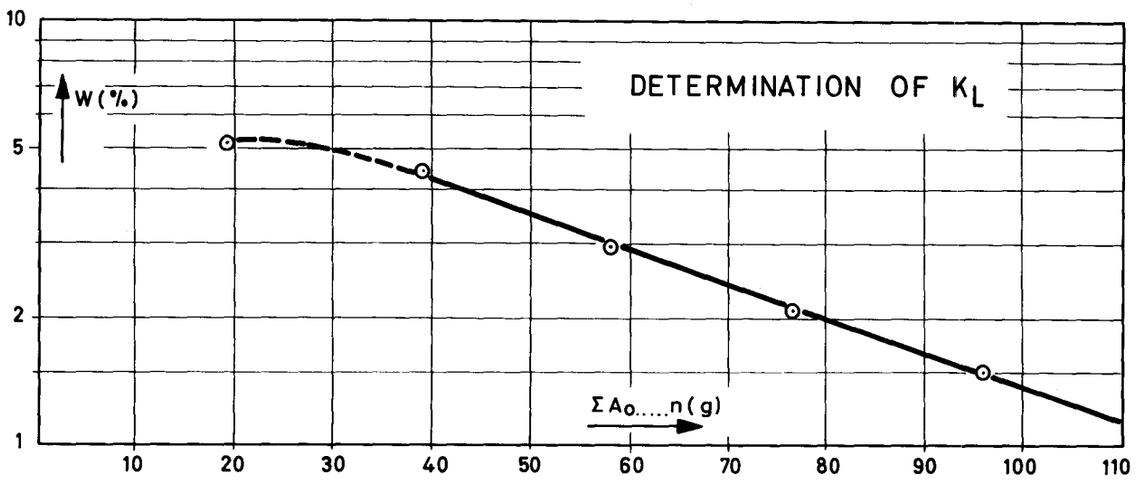


FIGURE 7


DETERMINATION OF K_L
W (%)
10
5
2
1
10
20
30
40
50
60
70
80
90
100
110
$\Sigma A_{o.....n}$ (g)

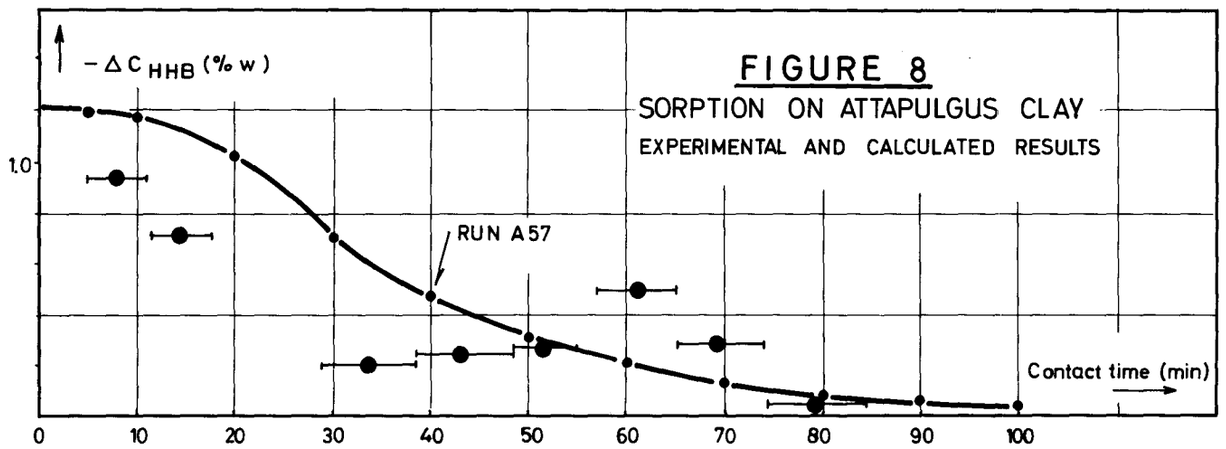
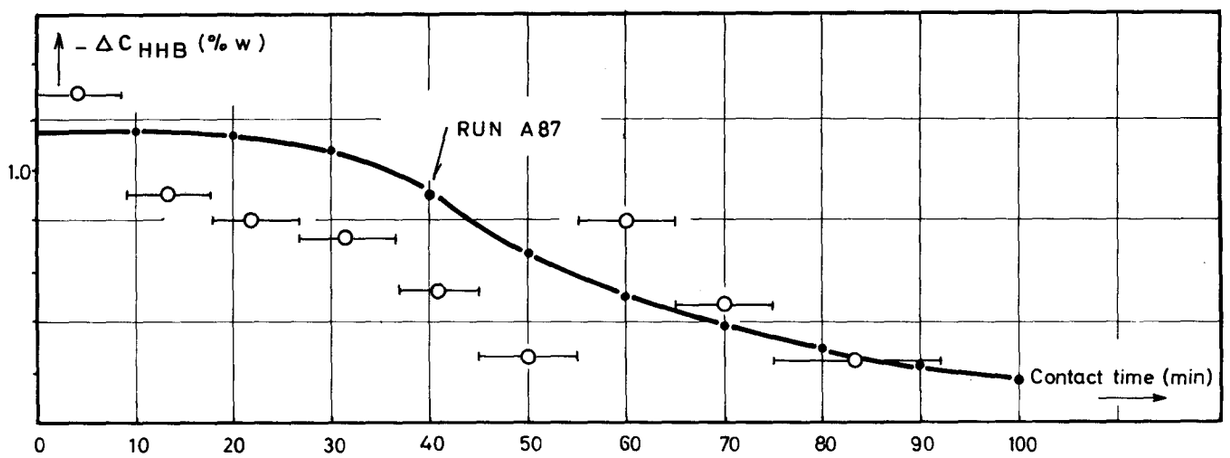


FIGURE 8
SORPTION ON ATTAPULGUS CLAY
EXPERIMENTAL AND CALCULATED RESULTS
$-\Delta C_{HHB}$ (% w)
1.0
RUN A57
Contact time (min)
0
10
20
30
40
50
60
70
80
90
100


$-\Delta C_{HHB}$ (% w)
1.0
RUN A87
Contact time (min)
0
10
20
30
40
50
60
70
80
90
100